Actinic Flux and Atmospheric Photolysis Frequency Measurements during INTEX-A

From

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Photochemical reactions provide the driving force for much of the chemistry in the atmosphere. The in situ rates of these photolysis reactions are important in understanding production and loss terms for the key atmospheric species odd hydrogen radicals and ozone. The first objective of this research is to deploy two scanning actinic flux spectroradiometer (SAFS) systems on the NASA DC-8 aircraft platform during the INTEX-A mission in the summer of 2004 to measure the in situ total spectral actinic flux as a function of wavelength and calculate the in situ photolysis frequencies of 23 important photochemical reactions. Photolysis frequencies for photodissociation reactions involving O_3, NO_2, CH_2O, HONO, HNO_3, N_2O_5, HO_2NO_2, PAN, H_2O_2, CH_3OOH, CH_3ONO_2, $CH_3CH_2ONO_2$, CH_3COCH_3, CH_3CHO, CH_3CH_2CHO, CHOCHO, CH_3COCHO, $CH_3CH_2CH_2CHO$, and $CH_3COCH_2CH_3$ will be calculated from the measured UV-VIS spectral actinic flux. These photolysis frequencies will be calculated using the absorption cross section and quantum yield data with temperature and pressure dependencies from the current NASA JPL data evaluation [*Sander et al.* 2003] and the most recent IUPAC recommendations for organic molecules [*Atkinson et al.* 2003].

The instrumentation, which has flown on the NASA DC-8 during the PEM-Tropics A, SONEX, PEM-Tropics B, SOLVE, and the TRACE P missions, will have an approximated detection limit of less than 0.1 μw/nm/cm^2 dependent on wavelength resulting in photolysis frequency detection limits of 2×10^{-7} sec^{-1} for $jO(^1D)$ and 1×10^{-7} sec^{-1} for jNO_2, all with a time response of 10 seconds.

In addition the investigators will deploy a newly developed actinic flux spectroradiometer system equipped with a monolithic monochromator with a cooled back thinned windowless CCD detector and a PC014+ based data acquisition and control system. The new system will have a time response of 1 HZ or better. This improved instrument response time will enable the accurate determination of actinic flux radiation in complex environments and allow investigators to study fast photochemical changes in and around clouds on future missions. This deployment is an engineering test of the technology being developed for future AURA validation activities on DC-8 and WB-57 aircraft platforms.

The investigators will perform NIST primary laboratory instrument calibrations, integrate all systems on the NASA DC-8, and deploy the two up and one down welling actinic flux spectroradiometers for the INTEX-A field mission at three field sites from June through August 2004. The instruments will be calibrated before each flight and preliminary data processed and submitted to the field data archive within 24 hours of each flight. Post mission calibrations will be preformed in the ARIM primary calibration facility. Final data for the spectral actinic flux as a function of wavelength and in situ photolysis frequencies of 23 important photochemical reactions will be submitted to the final data archive within six months for use by the science team.